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by

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13. ABSTRACT (Maximum 200 words) Octanitrocubane and 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane are predicted to be high-performance energetic materials; however neither compound has as yet been synthesized. In principle, they could be prepared by the cyclooligomerizations of dinitroacetylene and nitril cyanide, respectively. There is some encouraging chemical evidence that this may be feasible. The first steps in these processes might conceivably be cyclic dimerizations to form tetranitrocyclo-butadiene and 1,3-dinitro-2,4-diazacyclobutadiene. We have used a density functional computational procedure, B3P86/6-31G**, to analyze these proposed initial reactions. Optimized geometries and energies were calculated for dinitroacetylene and nitril cyanide, the two cyclic dimers, the intervening transition states, and also the desired ultimate products, the two cubanes. The activation barriers for the conversions of dinitroacetylene and nitril cyanide to the four-membered rings were found to be 47 and 45 kcal/mole, respectively, with the overall heats of reaction being -40 and +27 kcal/mole. The heats of reaction for proceeding from the starting materials to the final cubanes were -145 and +19 kcal/mole. The corresponding free energy changes were obtained, and are also negative for the dinitroacetylene processes and positive for the nitril cyanide. Thermodynamically, the cyclooligomerization of dinitroacetylene, whether to the dimer or to the cubane system, is predicted to be greatly favored over that of nitril cyanide.			
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CYCLOOLIGOMERIZATIONS AS POSSIBLE ROUTES TO CUBANE-LIKE SYSTEMS

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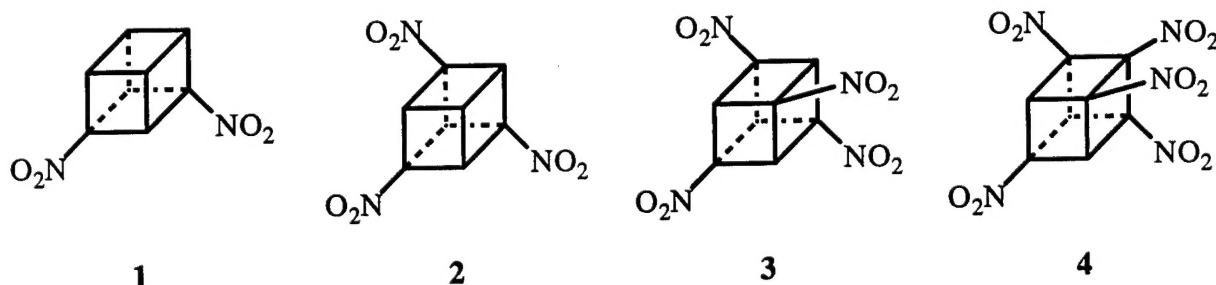
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INTRODUCTION

Polynitrocubanes continue to be of interest as potentially important high-energy compounds, e.g. explosives and propellants.¹⁻⁷ This is because cubane itself has a notably high crystal density for a hydrocarbon, 1.29 g/cm³,⁸ and also a high heat of formation, 129.5 kcal/mole in the solid phase and 148.7 kcal/mole in the gaseous.⁹ A further attractive feature is the remarkable stability shown by cubane,¹⁰ despite its very strained structure.

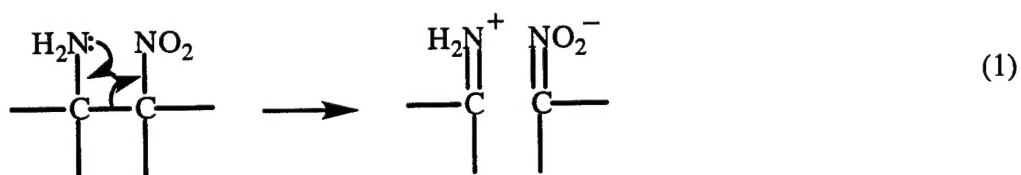
The density and the heat of formation are key factors in evaluating potential energetic performance,^{11,12} since they help to determine the rate of propagation of a detonation and the pressure behind the shock wave that is produced. The substitution of nitro groups can be anticipated to increase the density; for example, the experimental values for 1,3-dinitro-, 1,3,5-trinitro- and 1,3,5,7-tetranitrocubane (**1-3**) are 1.65, 1.74 and 1.81 g/cm³, respectively,¹² while that of the recently-prepared 1,2,3,5,7-pentanitrocubane (**4**) is 1.96 g/cm³.⁷ The latter is one of the highest densities known for a compound containing only carbons, hydrogens, oxygens



and nitrogens. The effect of nitro substituents upon the heat of formation is less straightforward. As shown in Table I, the molar value may increase, but it is likely to decrease on a gram basis, due to the added mass of the nitro groups. It is the latter value that is important for energetic performance.^{11,12}

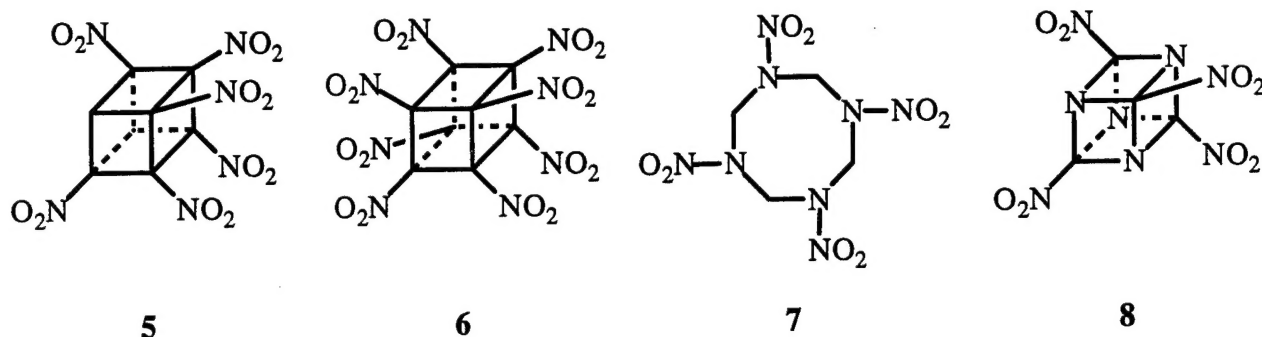
INSERT TABLE I ABOUT HERE.

Since approximately 1980, there have been continuing efforts to substitute nitro groups on the cubane framework; this has led successively to the preparation of **1**, **2** and **3**. (For reviews of this work, see Spear and Dagley⁶ and Lukin *et al.*⁷) In none of these molecules are there nitro groups on adjacent carbons; attempts to synthesize such analogues led to cleavage of the intervening C–C bond. This has been attributed to a “push-pull” mechanism operating in the course of the oxidation of the polyamine precursors:^{3,7}



(In computational analyses, we have shown that both nitro and amino substituents can *independently* produce a conformation-dependent weakening of neighboring C–C bonds in cubane,^{13,14} and that these effects may reinforce each other when the two groups are on adjacent carbons.)

Accordingly the introduction of a fifth NO₂ was achieved through the nitration of the anion of **3**.⁷ The pentanitrocubane **4** is currently the most highly nitrated cubane to have been prepared in pure form. A hexanitrocubane, **5**, has been reported,⁷ but has not yet been obtained free of solvent.



OCTANITROCUBANE AND 1,3,5,7-TETRANITRO-2,4,6,8-TETRAAZACUBANE

The ultimate objective of these efforts has generally been considered to be octanitrocubane, ^{6,6,7} Table II shows predictions of its properties relevant to energetic performance. For the most part, these are expected to be considerably superior to those of HMX, **7** (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), a very powerful current explosive that has long been taken as the standard against which new energetic materials, existing or proposed, are measured. Only in terms of its specific impulse (an indicator of propellant thrust) is octanitrocubane anticipated to not surpass HMX; this is probably because upon decomposition the former will (ideally) produce only 0.026 moles of gases (N_2 and CO_2) per gram of compound, compared to 0.041 (N_2 , CO and H_2O) for HMX. (The primary determinants of propellant thrust are the combustion temperature that is achieved and the moles of gaseous products per gram of propellant.^{15,16})

INSERT TABLE II ABOUT HERE.

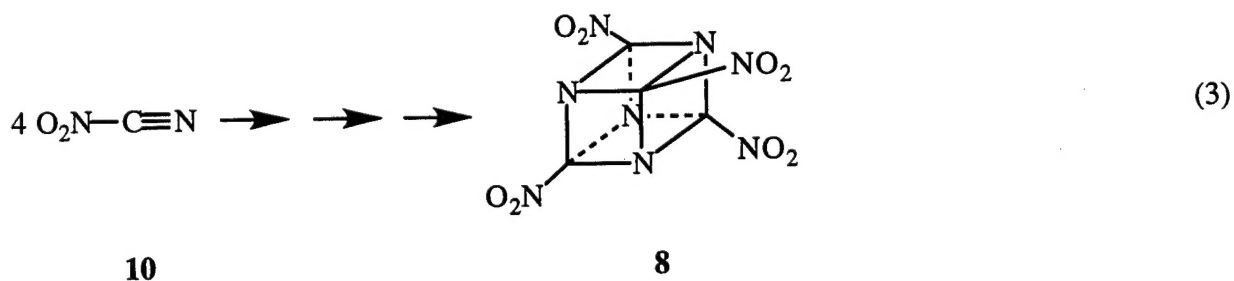
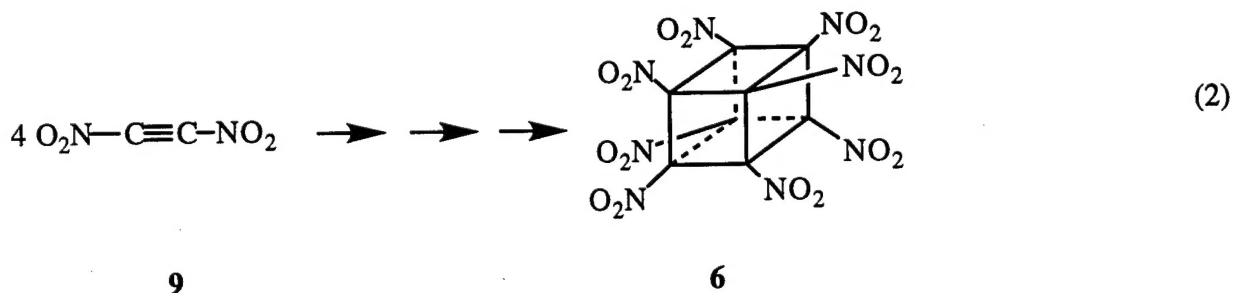
Attention has also been drawn to 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane, **8**, as a potential energetic compound.^{12,13,17} Table II shows its predicted properties to be at least as good as those of octanitrocubane, and perhaps significantly better. The specific impulse of **8** is expected to exceed that of HMX even though the moles of gaseous products per gram (N_2 and CO_2) is still only 0.028, presumably because its large heat of formation would lead to a higher combustion temperature. The tetranitrotetraazacubane should also benefit from the stabilizing effect that we

have found to be associated with the presence of aza nitrogens in both strained and unstrained aliphatic and alicyclic molecules.^{13,18,19} (Alkorta *et al* have independently reached the same conclusion specifically for cubane and azacubanes.²⁰)

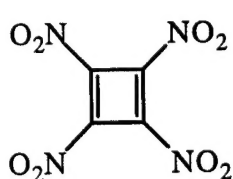
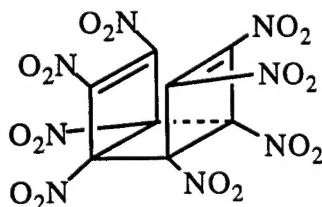
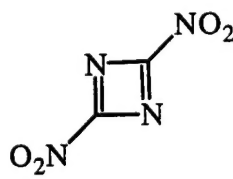
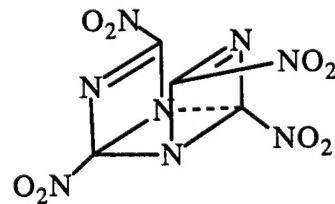
**CYCLOOLIGOMERIZATION PROCESSES: POSSIBLE ROUTES TO
OCTANITROCUBANE AND 1,3,5,7-TETRANITRO-2,4,6,8-
TETRAAZACUBANE.**

Background

In principle, octanitrocubane and 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane could be formed by the cyclooligomerizations of dinitroacetylene (**9**) and nitril cyanide (**10**), respectively:²¹

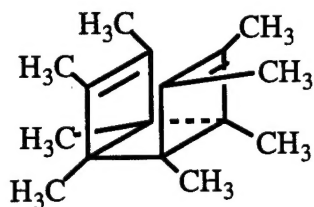


Each of these processes would probably involve several intermediates, perhaps including **11** and /or **12** in the case of eq. (2) and **13** and/or **14** in the case of eq. (3):

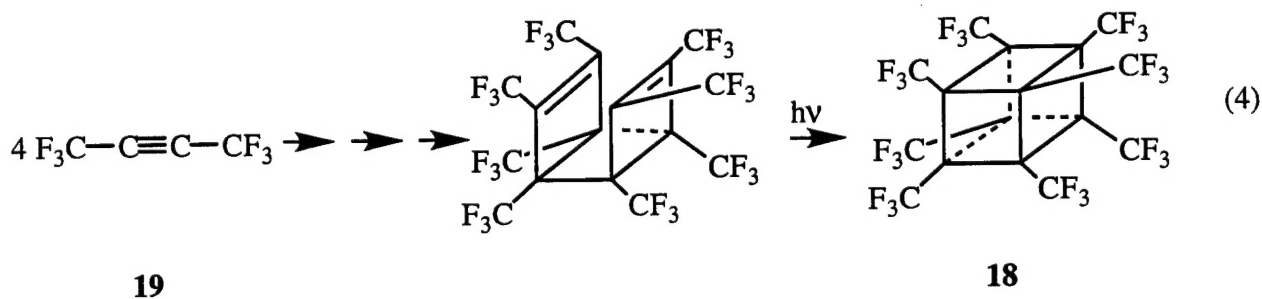
**11****12****13****14**

The molecules **11** and **13** can be viewed as cyclic dimers of dinitroacetylene and nitril cyanide, while **12** and **14** and the desired final products **6** and **8** can be regarded as cyclic tetramers.

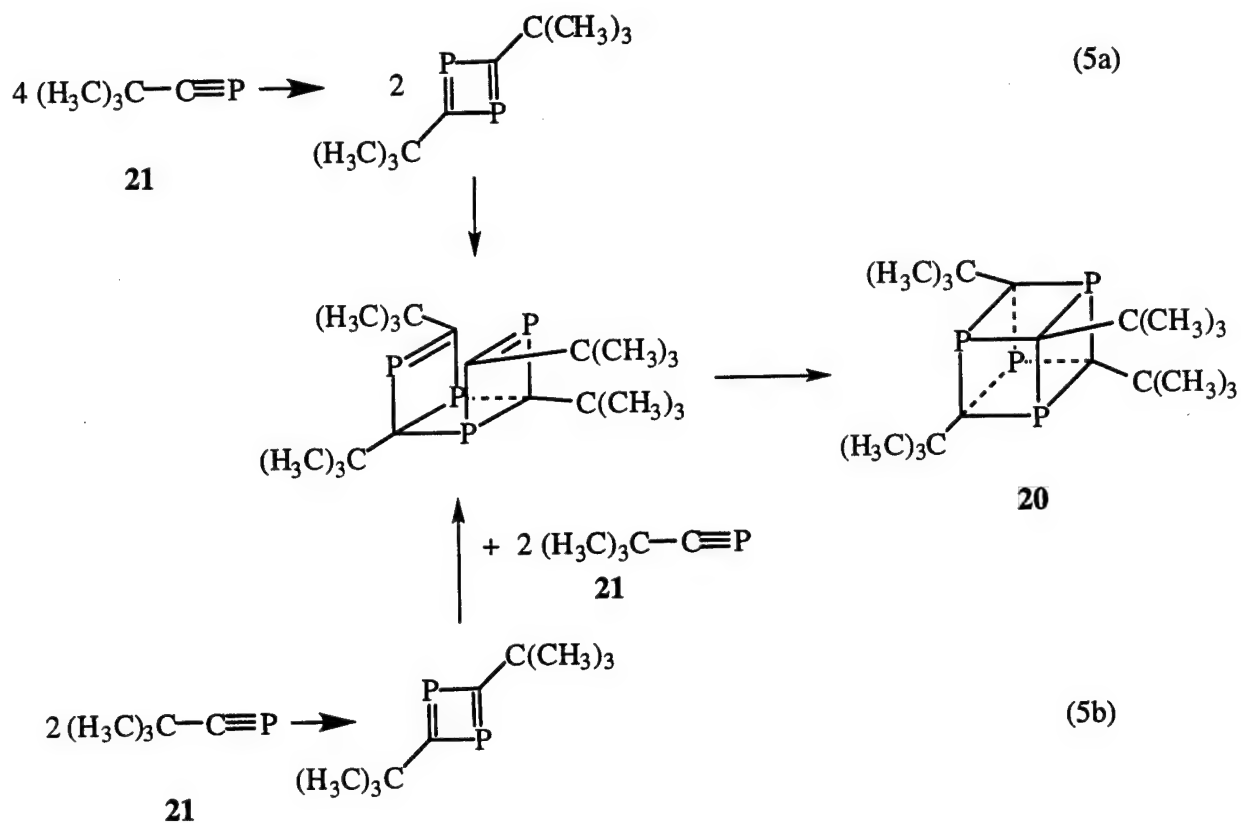
Some related efforts have already been made.²² The photolysis of the octadiene **15** or its octamethyl derivative **16** failed to produce cubane or octamethylcubane,²³⁻²⁵ nor did 1,3,5,7-cyclooctatetraene (**17**) yield cubane.²⁶

**15****16****17**

On the other hand, it has proven possible to prepare perfluorooctamethylcubane, **18**, from the acetylene derivative **19**,²⁷ by a series of chemical conversions followed by a final irradiation:



The fact that this does occur is particularly encouraging in the present context, since the CF_3 group is similar to the NO_2 in that both are strongly electron-withdrawing, primarily through induction.²⁸ More recently, the phosphacubane **20** has been synthesized by the thermal cyclooligomerization of the phosphalkyne **21**;²⁹ the mechanism was postulated to be either eq. (5a) or eq. (5b):



(The formation of phosphorous/carbon cage compounds from phosphalkynes is reviewed in the chapter by Mack and Regitz in this volume.) Finally, it was suggested some time ago,^{30,31} on the basis of infrared and Raman evidence, that a compound obtained^{30,32} by the ultraviolet irradiation of diphenylacetylene, $\text{H}_5\text{C}_6-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$, is octaphenylcubane.

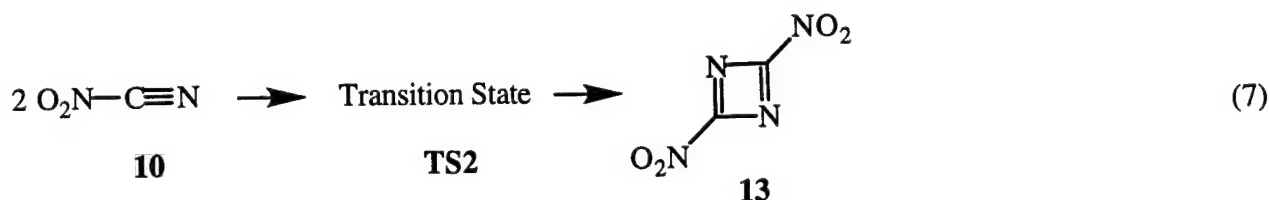
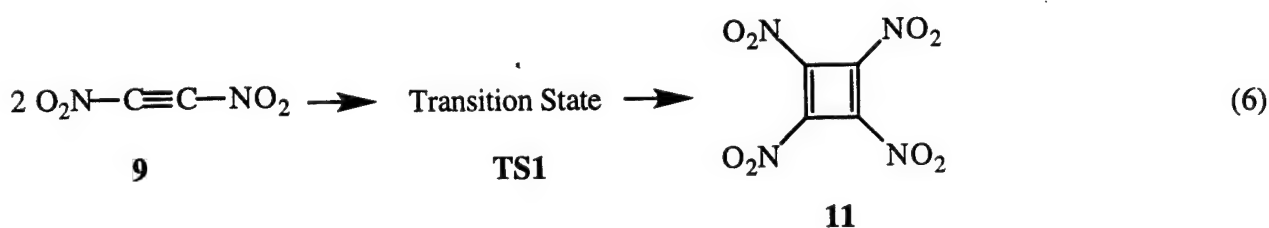
The starting compounds for the preparations of octanitrocubane and 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane by eqs. (2) and (3) are dinitroacetylene, **9**, and nitril cyanide, **10**. Dinitroacetylene has not yet been synthesized, although there are efforts in that direction;^{33,34} a computational investigation has shown that it does correspond to an energy minimum.³⁵ This has also been demonstrated for nitril cyanide,³⁶ and it has been reported to have been generated in the laboratory.³⁴

Computational Analyses

We have undertaken a computational investigation of the feasibilities of obtaining octanitrocubane and/or 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane by cyclooligomerization processes such as are depicted by eqs. (2) and (3). We are using a density functional procedure to assess the stabilities of possible intermediates and to seek the transition states leading to these and to the desired final products. Our objective is to determine whether reasonable routes can be established for either or both of these processes, involving attainable activation barriers.

The calculations are being carried out with the Gaussian 94 code,³⁷ using the Becke-3 (B3)³⁸ and Perdew-86 (P86)³⁹ functional combination and the 6-31G** basis set. Energy minima and transition states are confirmed by computing the vibration frequencies and verifying that there are, respectively, zero or one imaginary value.⁴⁰

Our focus has initially been upon the [2+2] cycloadditions shown in eqs. (6) and (7), which are conceivable first steps in the cyclooligomerization processes:

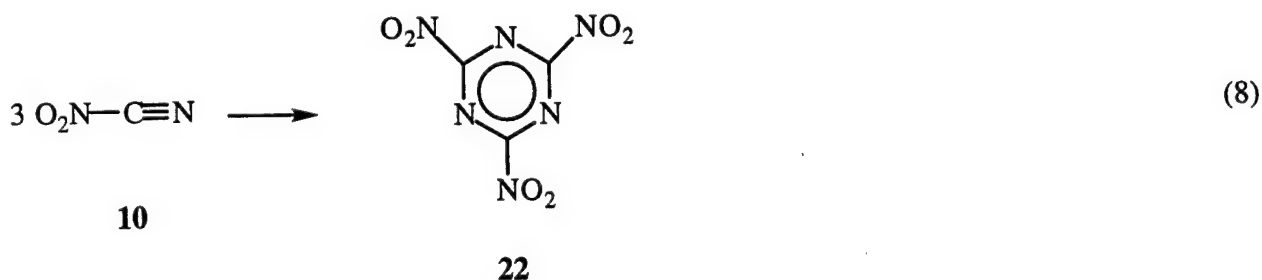


We computed optimized geometries for the reactants **9** and **10**, the possible intermediates **11** and **13**, and the desired final products, octanitrocubane (**6**) and 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane (**8**), and verified that these do correspond to energy minima (no imaginary vibration

frequencies). We also determined the structures of the transition states (one imaginary frequency), which can be a particularly time-consuming process since they are quite sensitive to the orientations of the reactants.

Our calculated reaction energetics for eqs. (6) and (7), as well as for the complete cyclooligomerizations represented by eqs. (2) and (3), are given in Table III. The heats of reaction were obtained from heats of formation computed by a modified version of a procedure described earlier.⁴¹

Table III shows the activation barriers for the conversion of dinitroacetylene and nitril cyanide to the four-membered rings **11** and **13** to differ by only about 2 kcal/mole; by the Arrhenius equation, however, this is enough to make the cyclodimerization of nitril cyanide at 298 K an order of magnitude faster than that of dinitroacetylene (other factors being equal). In contrast to the activation energies, the heats of reaction for these processes differ considerably, as is also the case for the complete cyclooligomerizations to the final products **6** and **8** (Table III). The dimerization and tetramerization of dinitroacetylene to form **11** and **6** are both exothermic, while the corresponding processes involving nitril cyanide going to **13** and **8** are both endothermic. The latter results are particularly striking because Korkin and Bartlett, using an MBPT(2) procedure, found the cyclic trimerization of nitril cyanide, eq. (8), to be distinctly exothermic, $\Delta E(0\text{ K}) = -70.2\text{ kcal/mole}$.⁴²



The significant energy release that accompanies the formation of **22** (unlike **13** and **8**) is presumably due to its aromatic stabilization.

INSERT TABLE III HERE.

The fact that the heats of reaction for the formation of **11** and **6** are so much more negative than for **13** and **8** does not contradict our earlier statement that aza nitrogens have a stabilizing effect. In molecules **13** and **8**, this stabilization is a decrease in the strain energy associated with the molecular framework, when referenced to an equivalent group of unstrained C-N and C-H bonds.¹⁹ The ΔH values in Table III, on the other hand, are referenced to the enthalpies of dinitroacetylene and nitril cyanide.

Table IV presents some computed structural data for the reactants, products and transition states in eqs. (6) and (7). The most interesting feature of these pertains to the transition state, **TS2**, in which the distance between the carbons is only about 0.05 Å greater than the typical length of a C-C single covalent bond.⁴³ As this transition state rearranges to the product, the dinitrodiazacyclobutadiene **13**, the formation of the new C-N single bonds is accompanied by an increase in the C---C distance to 1.751 Å.

INSERT TABLE IV HERE.

DISCUSSION

The activation barriers for eqs. (6) and (7) are not prohibitively large, so that both reactions should be kinetically feasible. Thermodynamically, however, the ΔG values in Table III show that the cyclooligomerization of dinitroacetylene, whether to the dimer or the tetramer, is greatly favored over that of nitril cyanide. This suggests that the conversions of dinitroacetylene to **11** and **6** are likely to occur with better yields than those of nitril cyanide to **13** and **8**. This does not of course mean that 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane, **8**, is any less promising as an

energetic target compound, but only that cyclooligomerization as a preparative route may be better suited for octanitrocubane, 6.

A final point of interest is that the presence of the nitro groups has a favorable thermodynamic effect on these cyclooligomerizations. For eqs. (9) and (10),



which are analogues of eqs. (6) and (7), we find $\Delta H(298 \text{ K}) = -6$ and 52 kcal/mole , respectively.

For eq. (11),



the measured heats of formation of acetylene⁴⁴ and cubane⁹ give a gas phase experimental value of $\Delta H(298 \text{ K}) = -69.3 \text{ kcal/mole}$. For all three of these reactions, the $\Delta H(298 \text{ K})$ of the fully nitrated version, given in Table III, is considerably more negative.

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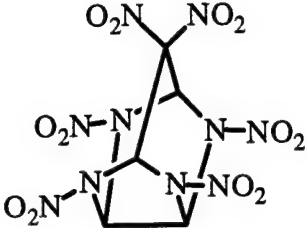
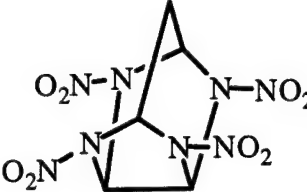
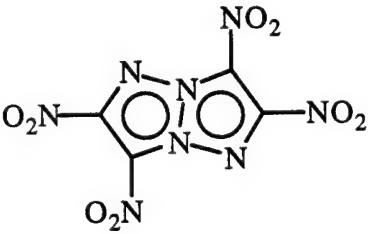
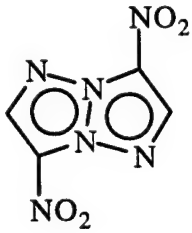
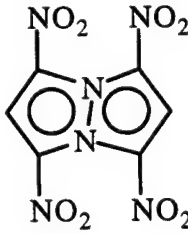
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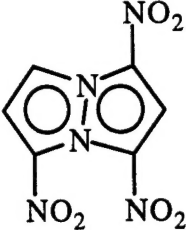
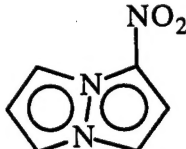
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Table I. Calculated solid phase heats of formation.^a

Compound	ΔH_f^{298K} (kcal/mole)	ΔH_f^{298K} (cal/g)
	62	157
	46	150
<hr/>		
	141	489
	114	573
<hr/>		
	78	273

(continued)

Table I. Calculated solid phase heats of formation (continued).^a

Compound	ΔH_f^{298K} (kcal/mole)	ΔH_f^{298K} (cal/g)
	67	276
	61	402

^aPolitzer, P., Grice, M. E. and Lane, P. unpublished results of density functional calculations. The procedure is described in reference 41.

Table II. Predicted properties of octanitrocubane, **6**, and 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane, **8**, and experimental values for HMX, **7**.

Property	Octanitrocubane, 6	1,3,5,7-Tetranitro-2,4,6,8-tetraazacubane, 8	HMX, 7
Crystal density, g/cm ³	2.09, ^a 2.125, ^b 2.21 ^c	2.19, ^a 2.086, ^b 2.05 ^c	1.902, ^d 1.905, ^d 1.96 ^e
Solid phase heat of formation, kcal/mole	81.0, ^a 144 ^f	158.0, ^a 189 ^f	17.9 ^e
Solid phase heat of formation, cal/g	175, ^a 310 ^f	548, ^a 655 ^f	60.4 ^e
Detonation velocity, m/sec	9820 ^a	10,400 ^a	9110, ^d 9100 ^e
Detonation pressure, kbar	467 ^a	540 ^a	395 ^d
Specific impulse (relative to HMX)	0.96 ^g	1.12 ^g	1.00 ^g

^aReference 12. The results were obtained using the procedure of reference 11.

^bH. L. Ammon, unpublished.

^cCalculated using the procedure of Murray, J. S., Brinck, T. and Politzer, P. *Chem. Phys.* **1996**, 204, 289.

^dGibbs, T. R. and Popolato, A., Eds., *LASL Explosive Property Data*, University of California Press, Berkeley, 1980. The densities given are for the β -polymorph. The detonation velocity and pressure correspond to densities of 1.89 and 1.900 g/cm³, respectively.

^eReference 16. The detonation velocity corresponds to a density of 1.9 g/cm³.

^fPoltzer, P., Grice, M. E. and Lane, P. unpublished results of density functional calculations. The procedure is described in reference 41.

^gReference 15.

Table III. Calculated (B3P86/6-31G**) reaction energetics.

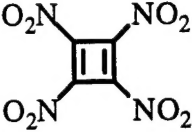
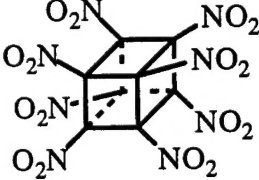
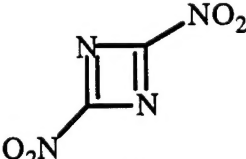
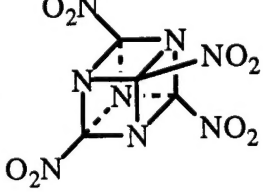
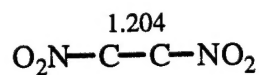
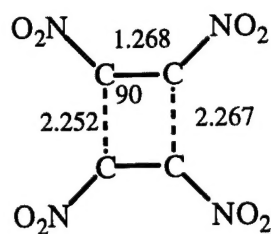
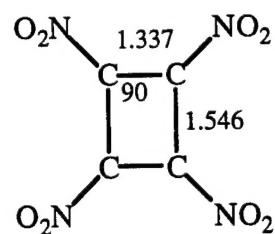
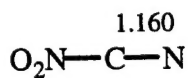
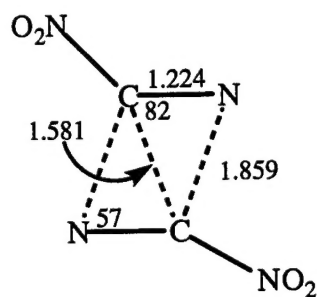
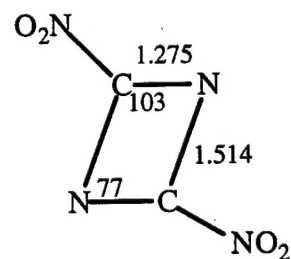
Reaction	$\Delta H(298\text{ K})$ kcal/mole	$\Delta G(298\text{ K})$ kcal/mole
$2 \text{ O}_2\text{N}-\text{C}\equiv\text{C}-\text{NO}_2 \longrightarrow \text{TS1}$ 9	47	
$2 \text{ O}_2\text{N}-\text{C}\equiv\text{C}-\text{NO}_2 \longrightarrow$  11	-40	-25
$4 \text{ O}_2\text{N}-\text{C}\equiv\text{C}-\text{NO}_2 \longrightarrow$  6	-145	-99
<hr/>		
$2 \text{ O}_2\text{N}-\text{C}\equiv\text{N} \longrightarrow \text{TS2}$ 10	45	
$2 \text{ O}_2\text{N}-\text{C}\equiv\text{N} \longrightarrow$  13	27	38
$4 \text{ O}_2\text{N}-\text{C}\equiv\text{N} \longrightarrow$  8	19	59

Table IV. Computed (B3P86/6-31G**) structural data.^a**9****TS1****11****10****TS2****13**^aDistances are in Angstroms, angles in degrees.